*Glass and Ceramics*, Vol. 68, Nos. 7 – 8, November, 2011 (Russian Original, Nos. 7 – 8, July – August, 2011)

UDC 666.7/.72

# LIGHT-TONE CERAMIC FACING BRICK MANUFACTURE USING FERROUS-METALLURGY BY-PRODUCTS

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Translated from *Steklo i Keramika*, No. 8, pp. 11 – 13, August, 2011.

The principal variational regularities of the properties of ceramic samples obtained from compositions based on combinations of loam, semi-fireclays, and metallurgical slag are examined. The phase composition of and structure formation processes in wall ceramic have been investigated using high-precision modern equipment. The composition of ceramic mix making it possible to produce high-quality ceramic facing brick based on clay raw materials and ferrous-metallurgy by-products is presented.

***Key words:*** facing brick, metallurgy byproduct, loam, ceramic mix.

There is a demand for ceramic facing brick on the market for building ceramic. The comparatively small reserves of high-quality clays make it necessary to use resource-conserving technologies to manufacture ceramic brick, partially because inferior local clays and industrial wastes are used. There is promise in using various by-products in the production of building materials [1, 2]. This trend is important because the amount of industrial wastes produced and often shipped to special sites occupying enormous areas and degrading the environment is increasing every year.

The objective of the present work is to develop a ceramic mix for producing high-quality facing brick based on a combination of local inferior grade loam and semi-fireclays with metallurgy by-products and to study the post-kilning properties and processes of phase- and structure-forming wall ceramic obtained from the optimal mix composition.

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Low-melting semisiliceous loam from the Vlasov deposit (pH = 13.6) was used in these studies as plastic materials. To improve the moldability of the ceramic mixes and raise the quality of the kilned articles the loam was used in combination with mixes made from semi-fireclays from the Vladimirovskoe deposit "VKTG" JSC. The chemical composition of the components used is presented in Table 1. Because loam with an elevated concentration of iron oxide is present in the chemical composition, brightening additives containing a large amount of chromophore-oxides must be used in order to obtain brick with light tones. Ferrous-metallurgical waste (slag) formed during the refinement of steel was used as a non-plastic material and calcium-containing additive.

The optimal composition of a ceramic mix for manufacturing high-quality, light-tone, facing brick was formulated in two steps. First, the optimal quantity of semi-fireclay raw material was determined. This was done by means of a series of experiments in which the semi-fireclay content could be changed. The amount of semi-fireclay was varied on the ba-

**TABLE 1.** Chemical Composition of the Components

| Component | Content, wt.% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | $TiO_2$ | CaO | MgO | $Na_2O$ | $K_2O$ | $SO_3$ | other |
| Vlasovskoe loam | 56.09 | 5.23 | 12.76 | 0.75 | 8.57 | 3.02 | 1.09 | 1.55 | 0.65 | 10.26 |
| Vladimirovskoe-clay mixes: | | | | | | | | | | |
| VKN-2 | 61.77 | 1.45 | 23.09 | 1.11 | 0.27 | 0.61 | 0.30 | 2.11 | – | 9.03 |
| VKV-2 | 60.70 | 3.80 | 23.84 | 1.09 | 0.61 | 0.26 | 0.30 | 2.17 | – | 7.51 |
| Metallurgical slag | 40.48 | 4.43 | 1.00 | 0.94 | 44.80 | 3.80 | 0.61 | – | – | 3.70 |



0361-7610/11/0708-0247 

**TABLE 2.** Ceramic Mix Compositions

| Component | Component content, wt.%, in compositions | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1.0 | 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 2.0 | 2.1 | 2.2 | 2.3 | 2.4 | 2.5 |
| Vlasovskoe loam | 85 | 81 | 77 | 72.5 | 68 | 64 | 85 | 81 | 77 | 72.5 | 68 | 64 |
| Vladimirovskoe-clay mixes: | | | | | | | | | | | | |
| VKN-2 | 15 | 14 | 13 | 12.5 | 12 | 11 | – | – | – | – | – | – |
| VKV-2 | – | – | – | – | – | – | 15 | 14 | 13 | 12.5 | 12 | 11 |
| Metallurgical slag | – | 5 | 10 | 15.0 | 20 | 25 | – | 5 | 10 | 15.0 | 20 | 25 |

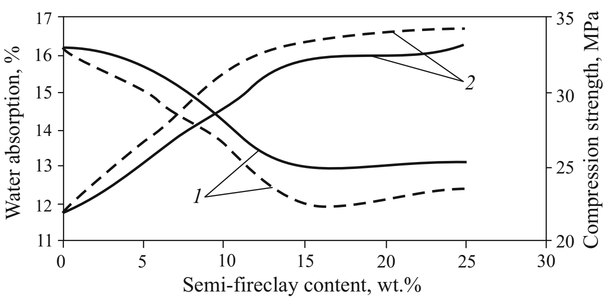


**Fig. 1.** Water absorption (*1*) and compression strength (*2*) for samples based on loam mix VKN-2 (——) and VKV-2 loam mix (– – –).

sis of the technological properties of the initial raw material and economic savings ranging from 5 to 25%.[2] Figure 1 displays the variation of the water absorption and compression strength of samples kilned at 1000°C.

According to Fig. 1 the compression strength of the samples increases considerably as the semi-fireclay content increases to 15%. The water absorption of the samples decreases in a regular manner to 13.0% with the addition of VKN-2 mix and to 12.0% with VKV-2 mix. Further increases of the content of semi-fireclay in the ceramic mix are undesirable because the strength and water absorption do not change much. For this reason, the ratio base loam : semi-fireclay = 85 : 15 was used in the present work.

The optimal composition of metallurgical slag introduced into the ceramic mix, making it possible to eliminate the negative factors of using loam — elevated shrinkage in air and low freeze resistance, was calculated at the second step. For this, a series of experiments using ceramic mixes whose compositions are presented in Table 2 was performed.

Component preparation prior to molding included grinding of the clay raw material in a ball mill to passage through a No. 09 sieve. The particle-size distribution of the metallurgical slag is dominated by grains smaller than 0.16 mm, making its comminution unnecessary.

The ceramic samples were molded by the plastic method with 22 – 25% moisture content of the mix. The molded samples were first dried at room temperature and then in a desiccator at 100 ± 5°C. Kilning was performed in a muffle furnace at 1000°C with isothermal soaking for 1 h. The physical-mechanical and operational properties were determined using standard procedures [3]; the ultimate compression strength was determined for cubic samples with 35 mm edge length; the shrinkage, water absorption, and freeze resistance were determined for plate-shaped samples with dimensions 60 × 30 × 14 mm. The results are presented in Table 3.

The data presented show that the water absorption of the samples containing 5 – 15% metallurgical slag conforms to GOST 530–2007 requirements for facing brick [4]. As the slag content increases, the air shrinkage indicator of the samples decreases. At the same time the fir shrinkage increases (to 2.3%), which attests to intensification of sintering. As the slag content increases to 15%, the ultimate compression strength and freeze resistance of the samples increase rapidly. Adding more slag to the ceramic mix (to 25%) does not greatly change the strength indicators. The freeze resistance decreases, while the water absorption exceeds 14%.

The introduction of metallurgical slag into the ceramic mix brightens fired paste, changing its color from red to beige and yellow, depending on the semi-fireclay which is

[2] Here and below, content by weight.

**TABLE 3.** Physical-Mechanical, Operational, and Aesthetic-User Properties

| Composition No. | Water absorption, % | Shrinkage, % | | Compression strength, MPa | Freeze resistance, number of cycles | Color |
|---|---|---|---|---|---|---|
| | | air | fire | | | |
| 1.0 | 13.0 | 6.1 | 1.4 | 32.2 | 40 | Rose |
| 1.1 | 13.1 | 5.7 | 1.5 | 36.7 | 43 | |
| 1.2 | 13.4 | 5.2 | 1.7 | 42.3 | 51 | Beige |
| 1.3 | 13.6 | 4.6 | 2.1 | 45.7 | 53 | |
| 1.4 | 14.6 | 4.3 | 2.3 | 46.1 | 48 | |
| 1.5 | 15.5 | 3.8 | 2.3 | 48.5 | 47 | |
| 2.0 | 12.0 | 6.5 | 1.3 | 33.3 | 38 | Red |
| 2.1 | 12.3 | 6.0 | 1.5 | 37.8 | 45 | Rose |
| 2.2 | 12.8 | 5.2 | 1.6 | 46.3 | 50 | |
| 2.3 | 13.5 | 4.5 | 1.8 | 48.4 | 51 | Yellow |
| 2.4 | 14.3 | 4.2 | 2.0 | 49.2 | 48 | Light yellow |
| 2.5 | 15.0 | 4.0 | 2.2 | 50.3 | 48 | |

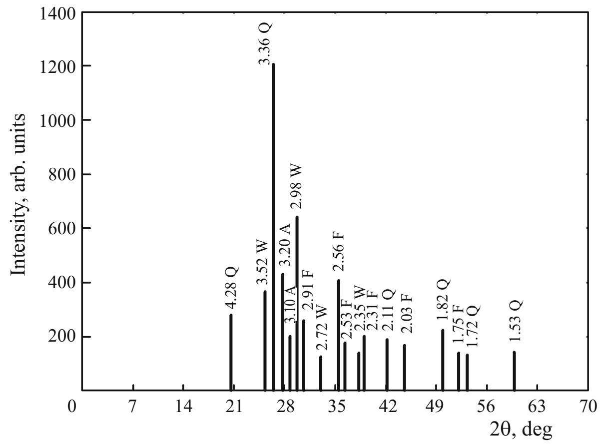


**Fig. 2.** X-ray diffraction pattern of kilned sample with composition 2.3: A) anortite, W) wollastonite, Q) quartz, F) fassaite.

introduced. When VKN-2 mix with low iron oxide content is used as the semi-fireclay raw material, the sample colors change radically with 10% slag addition. When VKV-2 mix with a high content of iron oxide is used to obtain samples with a uniform yellow color, the slag addition must be at least 15%. When still more waste is added (to 20 – 25%) fired paste with a uniform light yellow color is observed in the samples. Thus, the difference in the color of samples based on the VKN-2 and VKV-2 mixes and the amount of slag required to stabilize the color are explained by the different content of iron oxide in their chemical composition. The computed iron-calcium ratio $Fe_2O_3/CaO$ varies from 0.40 to 0.28 for the compositions 1.2 – 1.5 and from 0.38 to 0.30 for the compositions 2.3 – 2.5.

The XPA results obtained with an ARL X'TRA diffractometer (USA – Switzerland) for sample 2.3 established that hematite is absent from its phase composition. The following crystal phases were identified in its phase composition: β-quartz, anortite, wollastonite, and fassaite as well as an intense, fixed halo indicating an elevated content of a glassy phase (Fig. 2). Hematite is absent because it is included in the fassaite composition.

A synchronous thermal analysis was performed on a NETZSCH STA 449 C Jupiter differential analyzer. The temperature rise rate was taken to be 10 K/min, the temperature measurement range extended from 25 to 1000°C, and the medium in the furnace was air. Heating was performed in a corundum crucible. The thermal analysis was conducted using samples with the compositions 2.0 (base) and 2.3 (optimal). The DTA curve of sample 2.0 is characterized by the following endothermal effects: 132.3°C — removal of adsorption water; 478.0, 546.2, and 712.1°C — removal of crystallization water from clayey minerals; 805.2°C — dissociation of calcium carbonate. The following endothermal effects are present on the DTA curve of sample 2.3: 130.8°C — removal of adsorption water; 482.3, 550.6, and 718.3°C — removal of crystallization water from clayey minerals; 786.0°C — dissociation of calcium carbonate. Two exothermal effects are observed: 915.3°C — formation of anortite and 970.1°C — crystallization of wollastonite.

The advantage of using metallurgical slag in ceramic mixes as a brightening additive is that unlike carbonate rocks (marl, lime, chalk) it is a silicate material (80 – 85% $\gamma$-$Ca_2SiO_4$), which makes it possible to decrease the negative effect of the decarbonization process on the formation of a ceramic matrix during sintering at comparatively low temperatures (950 – 100°C).

In summary, it can be concluded on the basis of the data obtained that the introduction of 15% metallurgical slag into course-grain ceramic mixes based on loam and initial materials consisting of VKN-1 and VKV-2 semi-fireclays from the Vladimirovskoe deposit makes it possible to increase the strength and the operational and aesthetic-user properties of facing brick. Metallurgical slag functions as an inert and fluxing component, intensifying the sintering of the ceramic matrix and formation of new phases.

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